

Adsorption of Reactive Particles on a Random Catalytic Chain: An Exact Solution.

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Abstract

We study equilibrium properties of a catalytically-activated annihilation $A + A \rightarrow 0$ reaction taking place on a one-dimensional chain of length N ($N \rightarrow \infty$) in which some segments (placed at random, with mean concentration p) possess special, catalytic properties. Annihilation reaction takes place, as soon as any two A particles land onto two vacant sites at the extremities of the catalytic segment, or when any A particle lands onto a vacant site on a catalytic segment while the site at the other extremity of this segment is already occupied by another A particle. Non-catalytic segments are inert with respect to reaction and here two adsorbed A particles harmlessly coexist. For both "annealed" and "quenched" disorder in placement of the catalytic segments, we calculate exactly the disorder-average pressure per site. Explicit asymptotic formulae for the particle mean density and the compressibility are also presented.

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1 Introduction.

In many industrial and technological processes the design of desired chemicals requires the binding of chemically inactive molecules, which recombine only when some third substance - the catalytic substrate - is present [1, 2]. Within the two past decades much effort has been put in understanding of the peculiarities of such catalytically-activated reactions (CARs). On one hand, much progress was made in answering the question why and how specific catalytic substrates promote reactions between chemically inactive molecules (see, e.g. Ref.[3]). On the other hand, considerable theoretical knowledge was gained from an extensive study of a particular reaction - the CO-oxidation in the presence of metal surfaces with catalytic properties [4] (for a recent review see, e.g., Ref.[5]). While the first aspect [3] sheds light on catalysation mechanisms and may allow the calculation of K_{el} - the rate at which two reactants react being in the vicinity of each other and a specific catalytic substrate, the results of Refs.[4] show that the mere knowledge of K_{el} is not sufficient. As a matter of fact, Refs.[4] have substantiated the emergence of an essentially different behavior as compared to the predictions of the classical, formal-kinetics scheme and have shown that under certain conditions such collective phenomena as phase transitions or the formation of bifurcation patterns may take place [4]. Prior to these works on catalytic systems, anomalous behavior was amply demonstrated in other schemes [6–8], involving reactions on contact between two particles at any point of the reaction volume (i.e., the "completely" catalytic systems). It was realized [6–8] that the departure from the text-book, formal-kinetic predictions is due to many-particle effects, associated with fluctuations in the spatial distribution of the reacting species. This suggests that similarly to such "completely" catalytic reaction schemes, the behavior of the CARs may be influenced by many-particle effects.

Apart from the many-particle effects, behavior of the CARs might be affected by the very structure of the catalytic substrate, which is often not well-defined geometrically, but must be viewed as being an assembly of mobile or localized catalytic sites or islands, whose spatial distribution is complex [1]. Metallic catalysts, for instance, are often disordered compact aggregates, the building blocks of which are imperfect crystallites with broken faces, kinks and steps. Usually only the steps are active in promoting the reaction and thus the effective catalytic substrate is the geometrical pattern formed by these steps. Another example is furnished by porous materials with convoluted surfaces, such as, e.g., silica, alumina or carbons. Here the effective catalytic substrate is also only a portion of the total surface area because of the selective participation of different surface sites to the reaction - closed pores or pores with very small, bottleneck entrances are inaccessible to many reacting molecules. Finally, for liquid-phase catalytically-activated reactions the catalyst can consist of active

groups attached to polymer chains in solution.

Such complex morphologies render the theoretical analysis difficult. As yet, only empirical approaches have been used to account for the impact of the geometrical complexity on the behavior of the CARs, based mostly on heuristic concepts of effective reaction order or on phenomenological generalizations of the formal-kinetic "law of mass action" (see, e.g. Refs.[1] and [2] for more details). In this way the parameters entering the equations describing the observables (say, the mean particles densities) are fixed by fits to experimental data and can deviate from the values prescribed by the stoichiometric relations of the reactions involved. The important outcome of such descriptions is that they provide an evidence of the existing correlations in the morphology of the chemically reactive environment. On the other hand, their shortcoming is that they do not explain the mechanisms underlying the anomalous kinetic and stationary behavior. In this regard, analytical studies of even somewhat idealized or simplified models, such as, for instance, the ones proposed in Refs.[4], are already highly desirable since such studies may provide an understanding of the effects of different factors on the properties of the CARs.

In this paper we study the properties of catalytically-activated annihilation $A + A \rightarrow 0$ reaction in a simple, one-dimensional model with random distribution of the catalyst, appropriate to the just mentioned situation with the catalytically-activated reactions on polymer chains. More specifically, we consider here the $A + A \rightarrow 0$ reaction on a one-dimensional regular lattice which is brought in contact with a reservoir of A particles. Some portion of the intersite intervals (thick black lines in Fig.1) on the regular lattice possesses special "catalytic" properties such that they induce an immediate reaction $A + A \rightarrow 0$, as soon as two A particles land onto two vacant sites at the extremities of the catalytic segment, or an A particle lands onto a vacant site while the site at the other extremity of the catalytic segment is already occupied by another A particle.

We present here an exact solution of this model in two cases - a case when disorder in placement of the catalytic segments can be viewed as *annealed*, and a more complex situation with a *quenched* random distribution of the catalytic segments, and show that despite the apparent oversimplified nature of the model it exhibits an interesting non-trivial behavior. A brief account of these results has been presented in our earlier short publication [9]. We note finally that kinetics of $A + A \rightarrow 0$ reactions involving diffusive A particles which react upon encounters on randomly placed catalytic sites has been discussed already in Refs.[10, 11] and [12], and a rather surprising behavior has been found, especially in low-dimensional systems. Additionally, steady-state properties of $A + A \rightarrow 0$ reactions between immobile A particles with long-range reaction probabilities in systems with external particles input have been presented in Refs.[13] and [14] and revealed non-trivial ordering phenomena with anomalous

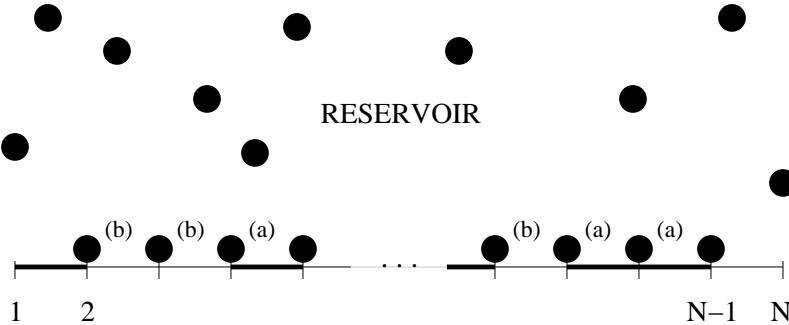


Figure 1: One-dimensional lattice of adsorption sites in contact with a reservoir. Filled circles denote hard-core A particles. Thick black lines denote the segments with catalytic properties. (a) denotes a "forbidden" particle configuration, which corresponds to immediate reaction. (b) depicts the situation in which two neighboring A particles may harmlessly coexist.

input intensity dependence of the mean particle density, which agrees with early experimental findings [15]. For completely catalytic 1D systems, kinetics of $A + A \rightarrow 0$ reactions with immobile A particles undergoing cooperative desorption have been discussed in Refs.[16, 17] and [18]. Exact solutions for $A + A \rightarrow 0$ reactions in 1D completely catalytic systems in which A particles perform conventional diffusive or subdiffusive motion have been presented in Refs.[19] and [20], respectively.

This paper is structured as follows: in section 2 we define the model and introduce basic notations. In section 3 we focus on the case of *annealed* disorder and derive exact closed-form expressions for the pressure per site, as well as present explicit asymptotic expansions in powers of the activity for the mean particle density and the compressibility. In section 4 we examine the case of *quenched* disorder. Here, we show that the thermodynamic limit result for the disorder-averaged pressure per site can be obtained very directly by noticing a similarity between the expressions defining the pressure in the model under study and the Lyapunov exponent of a product of random two-by-two matrices, obtained by Derrida and Hilhorst [21]. We also derive an explicit expression obeyed by the averaged logarithm of the partition function, which is valid for any chain's length N , and present its large- N expansion; we show, in particular, that the first correction to the thermodynamic limit result for the disorder-averaged pressure per site is proportional to the first negative power of N . Explicit asymptotic expansions for the mean particle density and the compressibility are also derived. Finally, in section 5 we conclude with a brief summary of our results and discussion.

2 The model.

Consider a one-dimensional regular lattice of unit spacing comprising N adsorption sites in contact with a reservoir (vapor phase) of identical, non-interacting hard-core A particles (see, Fig.1). The reservoir is steadily maintained at a constant pressure.

The A particles from the vapor phase can adsorb onto vacant adsorption sites and desorb back to the reservoir. The occupation of the " i "-th adsorption site is described by the Boolean variable n_i , such that

$$n_i = \begin{cases} 1, & \text{if the } i\text{-th site is occupied,} \\ 0, & \text{otherwise.} \end{cases}$$

Suppose next that some of the segments - intervals between neighboring adsorption sites possess "catalytic" properties (thick black lines in Fig.1) in the sense that they induce an immediate reaction $A + A \rightarrow 0$, as soon as two A particles land onto two vacant sites at the extremities of the catalytic segment, or an A particle lands onto a vacant site at one extremity of the catalytic segment while the site at the other extremity of this segment is already occupied by another A particle. Two reacted A particles instantaneously leave the lattice (desorb back to the reservoir). Any two A particle adsorbed at extremities of a non-catalytic segment harmlessly coexist.

To specify the positions of the catalytic segments, we introduce the quenched variable ζ_i , so that $\zeta_0 = \zeta_N = 0$ and

$$\zeta_i = \begin{cases} 1, & \text{if the } i\text{-th interval is catalytic, } i = 1, 2, \dots, N-1, \\ 0, & \text{otherwise.} \end{cases}$$

Now, for a given distribution of the catalytic segments, the partition function $Z_N(\zeta)$ of the system under study can be written as follows:

$$Z_N(\zeta) = \sum_{\{n_i\}} z^{\sum_{i=1}^N n_i} \prod_{i=1}^{N-1} (1 - \zeta_i n_i n_{i+1}), \quad (1)$$

where the summation $\sum_{\{n_i\}}$ extends over all possible configurations $\{n_i\}$, while z denotes the activity,

$$z = \exp(\beta\mu), \quad (2)$$

μ being the chemical potential, which accounts for the reservoir pressure and for the particles' preference for adsorption. Note that $Z_N(\zeta)$ in Eq.(1) is a functional of the configuration $\zeta = \{\zeta_i\}$.

It might be instructive to remark that $Z_N(\zeta)$ can be also thought of as a one-dimensional version of models describing adsorption of hard-molecules [22–29], i.e. adsorption limited by

the "kinetic" constraint that any two of the molecules can neither occupy the same site nor appear on the neighboring sites. The most celebrated examples of such models are furnished by the so-called "hard-squares" model [22–26], or by the "hard-hexagons" model first solved exactly by Baxter [28].

These models exhibit phase transitions. The universal classification of phase transitions is known to depend on the dimensionality, the presence of further interactions and the way in which the lattice can be partitioned into sublattices. For bipartite lattices and interactions dominated by nearest-neighbor exclusion, the ordering transition is the result of competition between the two sublattice densities. The phase transition is thus associated with a breaking of the symmetry between these two sublattices. For geometrically more complex Baxter's hard-hexagon model, which consists of particles with the nearest-neighbor exclusion on the triangular lattice, the phase transition belongs to the three-state Potts model universality class, in accordance with the fact that the phase transition is associated with symmetry breaking involving three competing equivalent sublattice densities. For more discussion see Ref.[30].

In our case of the CARs on random catalytic substrates the nearest-neighbor exclusion constraint is introduced only locally, at some specified, randomly distributed intervals. Such locally frustrated models of random reaction/adsorption thus represent a natural and meaningful generalization of the well-studied exclusion models over systems with disorder. Of course, in this context two-dimensional situations are of most interest, but nonetheless it might be instructive to find examples of such models which can be solved exactly in one dimension.

Our main goal here is to calculate the disorder-average pressure per site:

$$P_{\infty}^{(quen)} = \frac{1}{\beta} \lim_{N \rightarrow \infty} \frac{1}{N} \left\langle \ln(Z_N(\zeta)) \right\rangle_{\zeta}, \quad (3)$$

where the angle brackets with the subscript ζ here and henceforth denote averaging over all possible configurations $\{\zeta_i\}$. In this case, we suppose that ζ_i are quenched, independent, randomly distributed variables with distribution

$$\rho(\zeta) = p\delta(\zeta - 1) + (1 - p)\delta(\zeta). \quad (4)$$

As well, we will consider the case when the disorder in placement of the catalytic segments can be viewed as *annealed* and the mean density of the catalytic segments is equal to p ; in this case, which requires much simpler analysis, the pressure per site is given by

$$P_{\infty}^{(ann)} = \frac{1}{\beta} \lim_{N \rightarrow \infty} \frac{1}{N} \ln \left(\left\langle Z_N(\zeta) \right\rangle_{\zeta} \right), \quad (5)$$

We note that such a situation can be realized in practice in case when the catalytic agents, modelled here as the catalytic segments, diffuse. On the other hand, an assumption of the

annealed disorder is often used as a meaningful "mean-field" approximation for systems with quenched disorder. Hence, it might be instructive to consider this case in order to check the behavior provided by such a mean-field approach against an exact solution in the quenched disorder case.

Once P_∞ are obtained, all other pertinent thermodynamic properties can be readily evaluated by differentiating P_∞ with respect to the chemical potential μ ; in particular, the disorder-average mean particle density n will be given by

$$n_\infty = \frac{\partial}{\partial \mu} P_\infty, \quad (6)$$

while the compressibility k_T obeys

$$k_T = \frac{1}{n_\infty^2} \frac{\partial n_\infty}{\partial \mu}. \quad (7)$$

We set out to show that for both *annealed* and *quenched* disorder cases, when ζ_i are independent, two-state random variables all these functions can be evaluated explicitly, in a closed form. We will distinguish between these two cases by assigning superscripts (*ann*) and (*quen*).

To close this section, we display the results corresponding to two "regular" cases: namely, when $p = 0$ and $p = 1$, which will serve us in what follows as some benchmarks. In the $p = 0$ all sites are decoupled, and one has the trivial Langmuir adsorption results:

$$P_\infty^{(lan)} = \frac{1}{\beta} \ln(1 + z), \quad n_\infty^{(lan)} = \frac{z}{1 + z}, \quad (8)$$

and

$$\beta^{-1} k_T^{(lan)} = \frac{1}{z}. \quad (9)$$

The "regular" case when $p = 1$ is a bit less trivial, but the solution can be still straightforwardly obtained. In this case, we have

$$P_\infty^{(reg)} = \frac{1}{\beta} \ln \left(\frac{\sqrt{1 + 4z} + 1}{2} \right), \quad n_\infty^{(reg)} = 1 - \frac{2z}{1 + 4z - \sqrt{1 + 4z}}, \quad (10)$$

and

$$\beta^{-1} k_T^{(reg)} = \frac{2z}{\sqrt{1 + 4z}(1 + 2z - \sqrt{1 + 4z})}. \quad (11)$$

Note that in the $p = 1$ case (the completely catalytic system) the mean particle density tends to $1/2$ as $z \rightarrow \infty$ (compared to $n_\infty^{(lan)} \rightarrow 1$ behavior observed for the Langmuir case), which means that the adsorbent undergoes "ordering" transition and particles distribution on the lattice becomes periodic revealing a spontaneous symmetry breaking between two sublattices. In the limit $z \rightarrow \infty$ the compressibility vanishes as $k_T^{(reg)} \propto 1/\sqrt{z}$ compared to the Langmuir behavior $k_T^{(lan)} \propto 1/z$.

3 Annealed Disorder.

We start our analysis of the random reaction/adsorption model considering first the situation in which the disorder in placement of the catalytic segments can be viewed as *annealed*. In this case, the disorder-averaged pressure per site is defined by Eq.(5) and thus has a more simple form than that in Eq.(3), since we have to perform averaging not of the logarithm of the partition function in Eq.(1) but of the partition function itself.

Averaging of the partition function in Eq.(1) over the distribution of the catalytic segments can be performed very directly and yields

$$Z_N = \left\langle Z_N(\zeta) \right\rangle_\zeta = \sum_{\{n_i\}} z^{\sum_{i=1}^N n_i} \prod_{i=1}^{N-1} (1 - p n_i n_{i+1}). \quad (12)$$

Since $(1 - p n_i n_{i+1}) \equiv \exp(\ln(1 - p) n_i n_{i+1})$, the result in the latter equation can be thought of as a partition function of a one-dimensional lattice gas with nearest-neighbour repulsive interactions of amplitude $\ln(1/(1 - p))$. Note that here the original constraint that no two particle can be located simultaneously at the extremities of the catalytic segments is replaced by a more tolerant condition that the particles may occupy neighboring sites anywhere, but the penalty of $2 \ln(1 - p)$ has to be paid. For any finite $p < 1$ this penalty can be overpassed by increasing the chemical potential and hence, for large z one may thus expect completely different behavior in the annealed and quenched disorder cases. On the other hand, for $p = 1$ this penalty gets infinitely large and thus $p = 1$ is a special point.

Now, to find an explicit form of Z_N we proceed as follows. Let us first introduce an auxiliary, constrained partition function of the form

$$Z'_N = Z_N|_{n_N=1} = z \sum_{\{n_i\}} z^{\sum_{i=1}^{N-1} n_i} \prod_{i=1}^{N-2} (1 - p n_i n_{i+1}) (1 - p n_{N-1}), \quad (13)$$

i.e. Z'_N stands for the partition function of a one-dimensional lattice gas with a nearest-neighbor repulsion and fixed occupation of the site $i = N$, $n_N = 1$. Evidently, we have that

$$Z_N = Z_{N-1} + Z'_N. \quad (14)$$

Next, considering two possible values of the occupation variable n_{N-1} , i.e. $n_{N-1} = 0$ and $n_{N-1} = 1$, we find that Z'_N can be expressed through Z_{N-2} and Z'_{N-1} as

$$\begin{aligned} Z'_N &= z \sum_{\{n_i\}} z^{\sum_{i=1}^{N-2} n_i} \prod_{i=1}^{N-3} (1 - p n_i n_{i+1}) + \\ &+ z^2(1 - p) \sum_{\{n_i\}} z^{\sum_{i=1}^{N-2} n_i} \prod_{i=1}^{N-3} (1 - p n_i n_{i+1}) (1 - p n_{N-2}) = \\ &= z Z_{N-2} + z(1 - p) Z'_{N-1} \end{aligned} \quad (15)$$

Now, recursion in Eq.(14) allows us to eliminate Z'_N in Eq.(15). From Eq.(14) we have $Z'_N = Z_N - Z_{N-1}$, and consequently, we find from Eq.(15) that the unconstrained partition function Z_N in Eq.(12) obeys the following recursion

$$Z_N = \left(1 + z(1-p)\right)Z_{N-1} + zpZ_{N-2}, \quad (16)$$

which is to be solved subject to evident initial conditions

$$Z_0 \equiv 1 \quad \text{and} \quad Z_1 \equiv 1 + z. \quad (17)$$

Solution of the recursion in Eq.(16) can be readily obtained by standard means, i.e. evaluating the generating function for Z_N , $Z_t = \sum_{N=1}^{\infty} Z_N t^N$, and then inverting it with respect to the variable t , which yields

$$Z_N = \frac{(1 + zpt_+)}{zpt_+(t_+ - t_-)} t_+^{-N} - \frac{(1 + zpt_-)}{zpt_-(t_+ - t_-)} t_-^{-N}, \quad (18)$$

where

$$t_{\pm} = \pm \frac{1}{2zp} \sqrt{\left(1 + z(1-p)\right)^2 + 4zp} - \frac{\left(1 + z(1-p)\right)}{2zp} \quad (19)$$

Noticing next that $t_+ \leq |t_-|$ we find that in the annealed disorder case in the thermodynamic limit the disorder average pressure per site is given by

$$P_{\infty}^{(ann)} = -\frac{1}{\beta} \ln \left[\frac{1}{2zp} \sqrt{\left(1 + z(1-p)\right)^2 + 4zp} - \frac{\left(1 + z(1-p)\right)}{2zp} \right], \quad (20)$$

which expression is valid for any z and p .

Consider now the asymptotic small- z and large- z behavior of the pressure $P_{\infty}^{(ann)}$, the mean density $n_{\infty}^{(ann)}$ and the compressibility $k_T^{(ann)}$. Expanding $P_{\infty}^{(ann)}$ in Eq.(20) into the Taylor series in powers of the activity z , we find that in the small- z limit $P_{\infty}^{(ann)}$ follows:

$$\beta P_{\infty}^{(ann)} = z - \left(\frac{1}{2} + p\right)z + \left(\frac{1}{3} + 2p + p^2\right)z^3 - \left(\frac{1}{4} + 3p + \frac{9}{2}p^2 + p^3\right)z^4 + \mathcal{O}(z^5). \quad (21)$$

Note that $P_{\infty}^{(ann)}$ in Eq.(21) reduces to

$$\beta P_{\infty}^{(lan)} = z - \frac{1}{2}z + \frac{1}{3}z^3 - \frac{1}{4}z^4 + \mathcal{O}(z^5), \quad (22)$$

and

$$\beta P_{\infty}^{(reg)} = z - \frac{3}{2}z^2 + \frac{10}{3}z^3 - \frac{35}{4}z^4 + \mathcal{O}(z^5), \quad (23)$$

for $p = 0$ and $p = 1$, respectively. From Eq.(21) we find that in the annealed disorder case in the small- z limit the mean particle density is given by

$$n_{\infty}^{(ann)} = z - \left(1 + 2p\right)z^2 + \left(1 + 6p + 3p^2\right)z^3 - \left(1 + 12p + 18p^2 + 4p^3\right)z^4 + \mathcal{O}(z^5), \quad (24)$$

while the compressibility obeys

$$\beta^{-1}k_T^{(ann)} = \frac{1}{z} + p(2-p)z - 4pz^2 + 3p(2+3p)z^3 - 8p(1+4p+2p^2)z^4 + \mathcal{O}(z^5). \quad (25)$$

We consider next the asymptotic behavior of $P_\infty^{(ann)}$ in the large- z limit. We notice first that here $p = 1$ is actually a special point; that is, asymptotic large- z behavior of $P_\infty^{(ann)}$ is completely different for $p < 1$ and $p = 1$ (completely catalytic systems). For $p < 1$ and $z \gg (1-p)^{-2}$, we have that the asymptotic expansion of $P_\infty^{(ann)}$ reads

$$\begin{aligned} \beta P_\infty^{(ann)} &= \ln((1-p)^2 z) - \ln(1-p) + \frac{1}{(1-p)^2 z} - \frac{(1+2p)}{2(1-p)^4 z^2} + \\ &+ \frac{(1+6p+3p^2)}{3(1-p)^6 z^3} - \frac{(1+12p+18p^2+4p^3)}{4(1-p)^8 z^4} + \mathcal{O}(z^5), \end{aligned} \quad (26)$$

while in the regular, completely catalytic case $p = 1$ it follows

$$\beta P_\infty^{(ann)} = \beta P_\infty^{(reg)} = \frac{1}{2} \ln(z) + \frac{1}{2z^{1/2}} - \frac{1}{48z^{3/2}} + \frac{3}{1280z^{5/2}} + \mathcal{O}\left(\frac{1}{z^{7/2}}\right). \quad (27)$$

Consequences of such a difference can be seen in a dramatically different behavior of the mean particle density. For $p < 1$ and $z \gg (1-p)^{-2}$ we find

$$\begin{aligned} n_\infty^{(ann)} &= 1 - \frac{1}{(1-p)^2 z} + \frac{(1+2p)}{(1-p)^4 z^2} - \\ &- \frac{(1+6p+3p^2)}{(1-p)^6 z^3} + \frac{(1+12p+18p^2+4p^3)}{(1-p)^8 z^4} + \mathcal{O}(z^5), \end{aligned} \quad (28)$$

while in the regular case $p = 1$ the mean particle density is given by

$$n_\infty^{(reg)} = \frac{1}{2} - \frac{1}{4z^{1/2}} + \frac{1}{32z^{3/2}} - \frac{3}{512z^{5/2}} + \mathcal{O}(z^{-7/2}). \quad (29)$$

This signifies, in particular, that for p arbitrarily close but not equal to unity, the mean density is equal to 1 as $z = \infty$, while for p strictly equal to unity the mean density $n_\infty^{(ann)} = 1/2$. The behavior of $n_\infty^{(ann)}$ as a function of z for different values of p is depicted in Fig.3.

In a similar fashion we find that asymptotic behavior of the compressibility k_T is very different for $p < 1$ and $p = 1$. For $p < 1$ and $z \gg (1-p)^{-2}$, $k_T^{(ann)}$ obeys

$$\begin{aligned} \beta^{-1}k_T^{(ann)} &= \frac{1}{(1-p)^2 z} - \frac{4p}{(1-p)^4 z^2} + \\ &+ \frac{3p(2+3p)}{(1-p)^6 z^3} - \frac{8p(1+4p+2p^2)}{(1-p)^8 z^4} + \mathcal{O}(z^{-5}), \end{aligned} \quad (30)$$

while for $p = 1$ and $z \gg 1$ it follows

$$\beta^{-1}k_T^{(reg)} = \frac{1}{2z^{1/2}} + \frac{1}{2z} + \frac{3}{16z^{3/2}} - \frac{5}{256z^{5/2}} + \mathcal{O}\left(\frac{1}{z^{7/2}}\right). \quad (31)$$

Finally, we realize that in the *annealed* disorder case for any fixed z the compressibility $k_T^{(ann)}$ appears to be a *non-monotonic* function of p . To see this, it suffices to notice that, first, $k_T^{(lan)} \leq k_T^{(reg)}$, i.e. for any fixed z the value of the compressibility for $p = 0$ is always less or equal to its value for $p = 1$. Second, one readily finds that in the vicinity of $p = 1$ the compressibility $k_T^{(ann)}$ obeys

$$\beta^{-1}k_T^{(ann)} = \beta^{-1}k_T^{(reg)} + \frac{4z^2}{(1+4z)^{3/2}}(1-p) + \mathcal{O}\left((1-p)^2\right), \quad (32)$$

i.e. for any z the value $k_T^{(reg)}$ corresponding to $p = 1$ is approached from above. Consequently, for any fixed z the compressibility $k_T^{(ann)}$ is a non-monotoneous function of the mean density p of the catalytic segments. Behavior of the compressibility $k_T^{(ann)}$ as a function of p for several different values of z is presented in Fig.4.

4 Quenched Disorder.

We turn now to the more complex situation with a quenched disorder, in which case, in order to define the disorder-averaged pressure, we have to perform averaging of the logarithm of the partition function in Eq.(1). Consequently, here we aim to determine the recursions obeyed by $Z_N(\zeta)$ and $\left\langle \ln(Z_N(\zeta)) \right\rangle_\zeta$.

4.1 Recursion relations for $Z_N(\zeta)$ and $\left\langle \ln(Z_N(\zeta)) \right\rangle_\zeta$.

We proceed here along essentially the same lines as in the previous section. We introduce first a constrained partition function of the form

$$Z'_N(\zeta) = Z_N(\zeta)|_{n_N=1} = z \sum_{\{n_i\}} z^{\sum_{i=1}^{N-1} n_i} \prod_{i=1}^{N-2} \left(1 - \zeta_i n_i n_{i+1}\right) \left(1 - \zeta_{N-1} n_{N-1}\right), \quad (33)$$

where $Z'_N(\zeta)$ now stands for the partition function of a system with fixed set $\zeta = \{\zeta_i\}$ and fixed occupation of the site $i = N$, $n_N = 1$. Similarly to Eq.(14), we have that $Z_N(\zeta)$ obeys

$$Z_N(\zeta) = Z_{N-1}(\zeta) + Z'_N(\zeta). \quad (34)$$

Next, considering two possible values of the occupation variable n_{N-1} , i.e. $n_{N-1} = 0$ and $n_{N-1} = 1$, we find that $Z'_N(\zeta)$ can be expressed through $Z_{N-2}(\zeta)$ and $Z'_{N-1}(\zeta)$ as

$$Z'_N(\zeta) = zZ_{N-2}(\zeta) + z(1 - \zeta_{N-1})Z'_{N-1}(\zeta), \quad (35)$$

which parallels the result in Eq.(15). Eliminating $Z'_N(\zeta)$ in Eq.(34), we find eventually that the unconstrained partition function $Z_N(\zeta)$ in Eq.(1) obeys the following recursion:

$$Z_N(\zeta) = \left(1 + z(1 - \zeta_{N-1})\right)Z_{N-1}(\zeta) + z\zeta_{N-1}Z_{N-2}(\zeta), \quad (36)$$

which is to be solved subject to the initial conditions in Eq.(17).

A conventional way (see, e.g. Ref.[31, 32]) to study linear random three-term recursions is to reduce them to random maps by introducing the Ricatti variable of the form

$$R_N(\zeta) = \frac{Z_N(\zeta)}{Z_{N-1}(\zeta)}. \quad (37)$$

In terms of this variable Eq.(36) becomes

$$R_N(\zeta) = \left(1 + z(1 - \zeta_{N-1})\right) + \frac{z\zeta_{N-1}}{R_{N-1}(\zeta)}, \quad \text{with } R_1(\zeta) \equiv R_1 = 1 + z, \quad (38)$$

which represents a random homographic relation. Once $R_N(\zeta)$ is defined for arbitrary N , the partition function $Z_N(\zeta)$ can be readily determined as the product,

$$Z_N(\zeta) = \prod_{i=1}^N R_i(\zeta), \quad (39)$$

and hence, the desired disorder-average logarithm of the partition function will be obtained as

$$\left\langle \ln Z_N(\zeta) \right\rangle_{\zeta} = \sum_{i=1}^N \left\langle \ln R_i(\zeta) \right\rangle_{\zeta} \quad (40)$$

Before we proceed further on, some comments on the recursion in Eq.(38) are in order. We recall first that, by definition, each quenched random variable ζ_i assumes only two values - 1 (with probability p) and 0 (with probability $1 - p$). Hence, we may formally rewrite the random homographic relation in Eq.(38) as

$$R_i(\zeta) = \begin{cases} 1 + z/R_{i-1}(\zeta), & \zeta_{i-1} = 1, \quad (\text{with probability } p), \\ 1 + z = R_1, & \zeta_{i-1} = 0, \quad (\text{with probability } 1 - p). \end{cases}$$

Note now that recursion schemes of quite a similar form have been discussed already in the literature in different contexts. In particular, two decades ago Derrida and Hilhorst [21] (see also Ref.[34] for a more general discussion) have shown that such recursions occur in the analysis of the Lyapunov exponent $F(\epsilon)$ of the product of random 2×2 matrices of the form

$$F(\epsilon) = \lim_{N \rightarrow \infty} \frac{1}{N} \left\langle \ln \left(\text{Tr} \left[\prod_{i=1}^N \begin{pmatrix} 1 & \epsilon \\ z_i \epsilon & z_i \end{pmatrix} \right] \right) \right\rangle_{\{z_i\}}, \quad (41)$$

where z_i are independent positive random variables with a given probability distribution $\rho(z)$. Equation (41) is related, for instance, to the disorder-average free energy of an Ising chain with nearest-neighbor interactions in a random magnetic field, described by the Hamiltonian

$$H' = -J' \sigma_1 \sigma_N - J' \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} - \sum_{i=1}^N h'_i \sigma_i, \quad (42)$$

in which one sets $J' = \ln(1/\sqrt{\epsilon})$ and $h'_i = \ln(1/\sqrt{z_i})$. As noticed in Ref.[21], the product in Eq.(41) also appears in the solution of a two-dimensional Ising model with row-wise random vertical interactions [35], the role of ϵ being played by the wavenumber θ . The recurrence scheme in Eq.(41) emerges also in such an interesting context as the problem of enumeration of primitive words with random errors in the locally free and braid groups [33]. Some other examples of physical systems in which the recursion in Eq.(41) appears can be found in [31].

Further on, Derrida and Hilhorst [21] have demonstrated that $F(\epsilon)$ can be expressed as

$$F(\epsilon) = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N \left\langle \ln R'_i \right\rangle_{\{z_i\}}, \quad (43)$$

where R'_i are defined through the recursion

$$R'_i = 1 + z_{i-1} + z_{i-1}(\epsilon^2 - 1)/R'_{i-1}, \quad \text{with } R'_1 = 1. \quad (44)$$

Moreover, they have shown that the model admits an exact solution when

$$\rho(z) = (1 - p)\delta(z) + p\delta(z - y), \quad (45)$$

i.e. when similarly to the model under study, z_i are independent, random two-state variables assuming only two values - y with probability p and 0 with probability $1 - p$. Supposing that when i increases, a stationary probability distribution $P(R')$ of the R'_i independent of i exists [36], Derrida and Hilhorst [21] have found the following exact result:

$$\begin{aligned} F(\epsilon) &= p \ln(1 + b) - p(2 - p) \ln\left(1 + b \frac{y - b}{1 - by}\right) + \\ &+ (1 - p)^2 \sum_{N=1}^{\infty} p^N \ln\left(1 + b \left(\frac{y - b}{1 - by}\right)^{N+1}\right), \end{aligned} \quad (46)$$

where

$$b = 1 + \frac{(1 - y)^2}{2\epsilon^2 y} \left[1 - \left(1 + 4 \frac{\epsilon^2 y}{(1 - y)^2} \right)^{1/2} \right]. \quad (47)$$

In particular, Eq.(46) shows a striking behavior in the $\epsilon \rightarrow 0$ limit; in this case, Derrida and Hilhorst [21] have demonstrated that for

$$py > 1, \quad \text{and } p < 1, \quad (48)$$

which implies that $\int \rho(z) \ln(z) < 0$, the Lyapunov exponent $F(\epsilon)$ defined by Eq.(46) exhibits an anomalous, singular behavior of the form

$$F(\epsilon) \sim \epsilon^\alpha, \quad \text{where } \alpha = -\ln(p)/\ln(y). \quad (49)$$

We turn now back to our recursion scheme in Eq.(38) and notice that setting

$$R_i(\zeta) = (1 + z) R'_i, \quad (50)$$

and choosing

$$y = -\frac{z}{1+z} = -n_{\infty}^{(lan)}, \quad \text{and} \quad \epsilon^2 = \frac{z}{1+z} = n_{\infty}^{(lan)}, \quad (51)$$

makes the recursion schemes in Eqs.(38) and (44) identic! Consequently, the disorder-average pressure per site in our random catalytic reaction/adsorption model can be expressed as

$$P_{\infty}^{(quen)} \equiv \frac{1}{\beta} \ln(1+z) + \frac{1}{\beta} F(\epsilon), \quad (52)$$

where $F(\epsilon)$ is the Lyapunov exponent of the product of random 2×2 matrices in Eq.(41), in which ϵ and z_i are defined by Eqs.(45) and (51).

Note next that the first term on the right-hand-side of Eq.(52) is a trivial Langmuir result for the $p = 0$ case (adsorption without reaction) which would entail $n_{\infty}^{(quen)} = z/(1+z)$. Hence, all non-trivial, disorder-induced behavior is embodied in the Lyapunov exponent $F(\epsilon)$. We hasten to remark, however, that despite some coincidence of results, the random reaction/adsorption model under study has completely different underlying physics, as compared to the model studied by Derrida and Hilhorst [21]. Thus, one would not expect any singular overall behavior of pressure in the $\epsilon \rightarrow 0$ limit (which corresponds here to the limit of vanishingly small activities z (or $\mu \rightarrow -\infty$), and thus pertains to $n \ll 1$). In consequence, here y is also dependent on z and $y \rightarrow 0$ in the same manner as ϵ . Moreover, in our case $y < 0$, which invalidates the condition in Eq.(48).

4.2 Disorder-averaged pressure.

The disorder-averaged pressure per site can be thus readily obtained from Eqs.(46) and (47) by defining the parameters y and ϵ as prescribed in Eq.(51). This yields the following explicit representation

$$\begin{aligned} \beta P_{\infty}^{(quen)} &= \ln(\phi_z) - (1-p) \ln(1-\omega^2) + \\ &+ \frac{(1-p)^2}{p} \sum_{N=1}^{\infty} p^N \ln(1 - (-1)^N \omega^{N+2}), \end{aligned} \quad (53)$$

where

$$\phi_z = \frac{1 + \sqrt{1+4z}}{2}, \quad (54)$$

and

$$\omega = \frac{\sqrt{1+4z} - 1}{\sqrt{1+4z} + 1} = z/\phi_z^2 = 1 - \frac{1}{\phi_z} \quad (55)$$

Note that ϕ_z obeys $\phi_z(\phi_z - 1) = z$ and thus for $z = 1$ the ϕ_1 is just the "golden mean", $\phi_1 = (\sqrt{5} + 1)/2$. Below we will show why and how this mathematical constant appears here.

On the other hand, the derivation of the result in Eq.(53) can be performed in a very straightforward manner without resorting to the assumption on existence of a stationary

probability distribution $P(R')$; the intermediate steps of such a derivation contain useful formulae, which might be helpful for the understanding of the asymptotic behavior of Eq.(53). Since it allows us to answer also the question of how the thermodynamic limit is achieved, we find it expedient to present such a derivation here.

We start with calculation of an explicit form of $\langle \ln R_i(\zeta) \rangle_\zeta$. To do it, it suffices to notice the following two points: First, we notice that

$$R_i(\zeta) = R_i(\zeta_{i-1}, \zeta_{i-2}, \zeta_{i-3}, \dots, \zeta_1), \quad (56)$$

and

$$R_{i-1}(\zeta) = R_i(\zeta_{i-2}, \zeta_{i-3}, \zeta_{i-4}, \dots, \zeta_1), \quad (57)$$

i.e. $R_{i-k}(\zeta)$ depends only on ζ_{i-k-n} with $n = 1, 2, \dots, i-k-1$ and is independent of ζ_{i-k} . Second, with probability $1-p$ the Ricatti variable is set equal to $1+z$, i.e. to its initial value R_1 , which is a non-random function. These two observations allow us to work out an explicit formula for $\langle \ln(R_i(\zeta)) \rangle_\zeta$ which is valid for any i .

Taking the logarithm of both sides of Eq.(38) and averaging it with respect to the distribution of random variables ζ_i , we have:

$$\langle \ln(R_i(\zeta)) \rangle_\zeta = \left\langle \ln \left(1 + z(1 - \zeta_{i-1}) + z \frac{\zeta_{i-1}}{R_{i-1}(\zeta)} \right) \right\rangle_\zeta. \quad (58)$$

We note next that since $R_{i-1}(\zeta)$ is independent of ζ_{i-1} , we can straightforwardly average the right-hand-side of Eq.(58) with respect to ζ_{i-1} , i.e.

$$\begin{aligned} \langle \ln(R_i(\zeta)) \rangle_\zeta &= \left\langle \ln \left(1 + z(1 - \zeta_{i-1}) + z \frac{\zeta_{i-1}}{R_{i-1}(\zeta)} \right) \right\rangle_\zeta = \\ &= (1-p) \ln(1+z) + p \left\langle \ln \left(1 + \frac{z}{R_{i-1}(\zeta)} \right) \right\rangle_\zeta = \\ &= (1-p) \ln(1+z) + \\ &+ p \left\langle \ln \left(1 + \frac{z}{1 + z(1 - \zeta_{i-2}) + z \frac{\zeta_{i-2}}{R_{i-2}(\zeta)}} \right) \right\rangle_\zeta. \end{aligned} \quad (59)$$

Now, since that $R_{i-2}(\zeta)$ is independent of ζ_{i-2} , we can again average over states of this

variable, which yields

$$\begin{aligned}
\left\langle \ln(R_i(\zeta)) \right\rangle_{\zeta} &= (1-p) \ln(1+z) + p \left\langle \ln \left(1 + \frac{z}{1+z(1-\zeta_{i-2}) + z \frac{\zeta_{i-2}}{R_{i-2}(\zeta)}} \right) \right\rangle_{\zeta} = \\
&= (1-p) \ln(1+z) + p(1-p) \ln \left(1 + \frac{z}{1+z} \right) + \\
&+ p^2 \left\langle \ln \left(1 + \frac{z}{1 + \frac{z}{R_{i-2}(\zeta)}} \right) \right\rangle_{\zeta} = \\
&= (1-p) \ln(1+z) + p(1-p) \ln \left(1 + \frac{z}{1+z} \right) + \\
&+ p^2 \left\langle \ln \left(1 + \frac{z}{1 + \frac{z}{1 + \frac{z}{R_{i-3}(\zeta)}}} \right) \right\rangle_{\zeta}. \tag{60}
\end{aligned}$$

Noticing again that $R_{i-3}(\zeta)$ is independent of ζ_{i-3} and etc., we arrive eventually at the following explicit representation for $\left\langle \ln(R_i(\zeta)) \right\rangle_{\zeta}$:

$$\left\langle \ln(R_i(\zeta)) \right\rangle_{\zeta} = (1-p) \sum_{n=1}^{i-1} p^{n-1} \mathcal{F}_n + p^{i-1} \mathcal{F}_i, \tag{61}$$

where the sum on the right-hand-side of Eq.(61) is defined for $i \geq 2$ and equals zero otherwise, while \mathcal{F}_n denote natural logarithms of the Stieltjes-type continued fractions of the form

$$\begin{aligned}
\mathcal{F}_1 = \ln(1+z), \quad \mathcal{F}_2 &= \ln \left(1 + \frac{z}{1+z} \right), \quad \mathcal{F}_3 = \ln \left(1 + \frac{z}{1 + \frac{z}{1+z}} \right), \\
&\dots \\
\mathcal{F}_i &= \ln \left(1 + \frac{z}{1 + \frac{z}{1 + \frac{z}{1 + \frac{z}{\dots}}}} \right). \tag{62}
\end{aligned}$$

To analyze the leading large- N behavior of the disorder-average pressure per site we resort to the standard generating function technique [37], often used, in particular, in the analysis of peculiar properties of different random walks [38]. Let us define first an auxiliary generating function

$$\mathcal{R}_t = \sum_{n=1}^{\infty} t^n \left\langle \ln(R_n(\zeta)) \right\rangle_{\zeta}. \tag{63}$$

Then, multiplying both sides of Eq.(61) by t^n and performing summation, we readily find that

$$\mathcal{R}_t \equiv \frac{1-pt}{p(1-t)} \sum_{n=1}^{\infty} t^n p^n \mathcal{F}_n. \tag{64}$$

Consequently, the generating function of the averaged logarithm of the partition function $Z_N(\zeta)$ obeys:

$$\begin{aligned}\mathcal{Z}_t &= \sum_{N=1}^{\infty} t^N \langle \ln Z_N(\zeta) \rangle_{\zeta} = \sum_{N=1}^{\infty} t^N \sum_{n=1}^N \left\langle \ln(R_n(\zeta)) \right\rangle_{\zeta} = \\ &= \frac{1}{1-t} \mathcal{R}_t = \frac{1-pt}{p(1-t)^2} \sum_{n=1}^{\infty} t^n p^n \mathcal{F}_n,\end{aligned}\tag{65}$$

and hence, the generating function of an average pressure per site, defined as

$$\mathcal{P}_t = \frac{1}{\beta} \sum_{N=1}^{\infty} \frac{t^N}{N} \langle \ln Z_N(\zeta) \rangle_{\zeta},\tag{66}$$

attains the form

$$\mathcal{P}_t = \frac{1}{\beta p} \sum_{N=1}^{\infty} p^N \mathcal{F}_N (I_N - p I_{N+1}),\tag{67}$$

where

$$I_N = \int_0^t d\tau \frac{\tau^{N-1}}{(1-\tau)^2}.\tag{68}$$

Now, in the large- N limit, the asymptotic behavior of the disorder-average pressure P_N per site in a finite chain of length N can be obtained very directly from the expansion of \mathcal{P}_t in the vicinity of the closest to the origin singular point [37], i.e. $t = 1$. Since, in the limit $t \rightarrow 1^-$, I_N obeys

$$I_N = \frac{1}{1-t} + (N-1) \ln(1-t) + \mathcal{O}(1),\tag{69}$$

we have that in this limit \mathcal{P}_t is given by

$$\mathcal{P}_t = \frac{1}{1-t} P_{\infty}^{(quen)} + \ln(1-t) \left(p \frac{\partial}{\partial p} P_{\infty}^{(quen)} \right) + \mathcal{O}(1),\tag{70}$$

where

$$P_{\infty}^{(quen)} = \frac{(1-p)}{\beta p} \sum_{n=1}^{\infty} p^n \mathcal{F}_n.\tag{71}$$

Consequently, we find that in the large- N limit $P_N^{(quen)}$ follows

$$P_N^{(quen)} = P_{\infty}^{(quen)} - \frac{1}{N} \left(p \frac{\partial}{\partial p} P_{\infty}^{(quen)} \right) + \mathcal{O}\left(\frac{1}{N^2}\right),\tag{72}$$

in which equation $P_{\infty}^{(quen)}$ in Eq.(71) is the desired thermodynamic limit result for the disorder-average pressure per site in the quenched disorder case. Note that in virtue of the expansion in Eq.(72), the corrections to the thermodynamic limit are proportional to the first inverse power of the chain length N . Note also that since

$$\lim_{n \rightarrow \infty} \mathcal{F}_n = \ln(\phi_z) = \ln\left(\frac{1 + \sqrt{1+4z}}{2}\right)\tag{73}$$

i.e. \mathcal{F}_n is the n -th approximant of $\ln(\phi_z)$, $P_\infty^{(quen)}$ can be thought of as the generating function of such approximants. One expects then that for $z < 1$ the sequence of approximants converges quickly to $\ln(\phi_z)$; expanding the n -th approximant \mathcal{F}_n into the Taylor series in powers of z , one has that the first n terms of such an expansion coincide with the first n terms of the expansion of $\ln(\phi_z)$. Consequently, \mathcal{F}_n and \mathcal{F}_{n-1} differ only by terms of order z^n , which signifies that convergence is good. On the other hand, for $z \geq 1$ convergence becomes poor and one has to seek for a more suitable representation. As a matter of fact, already for $z = 1$ one has that in the limit $n \rightarrow \infty$ the approximant \mathcal{F}_n tends to $\ln(\phi_1)$, i.e. the logarithm of the "golden mean", which is known as the irrational number worst approximated by rationals. Moreover, for $z \rightarrow \infty$ the convergence is irregular in the sense that only the approximants with odd numbers show the same large- z behavior as $\ln(\phi_z)$; the approximants with even n all tend as $z \rightarrow \infty$ to finite values $\ln(n/2 + 1)$ (see, Fig.2). We turn now back to the result

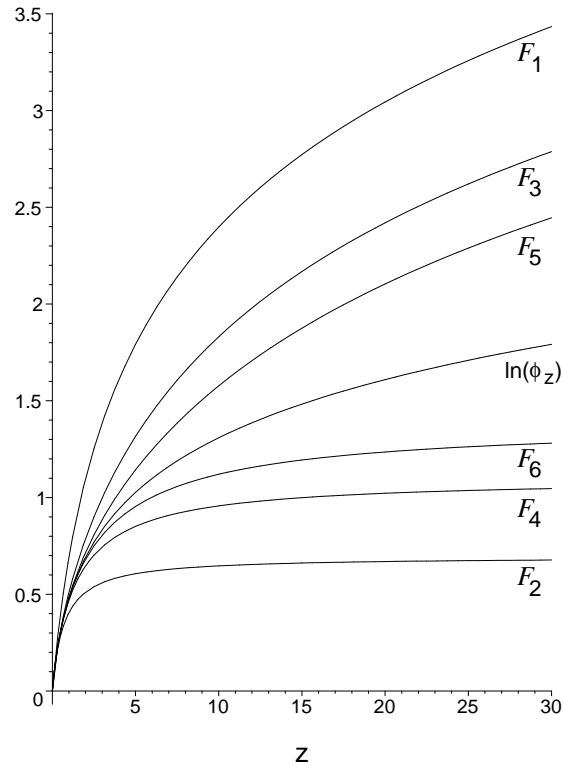


Figure 2: Plot of the approximants \mathcal{F}_n , $n = 1, 2, 3, 4, 5$ and 6 , and $\ln(\phi_z)$ versus activity z .

in Eq.(71) aiming to find a convenient representation more amenable for further analysis. To do this, let us note that \mathcal{F}_n in Eq.(62) can be expressed as the logarithm of the convergents

of the Stiltjes-type continued fractions:

$$\mathcal{F}_n = \ln \left(\frac{K_n(z)}{K_{n-1}(z)} \right), \quad (74)$$

where $K_n(z)$ are polynomials of the activity z defined through the three-term recursion¹

$$K_n(z) = K_{n-1}(z) + zK_{n-2}(z), \quad K_0(z) \equiv 1, \quad K_1(z) \equiv 1 + z. \quad (75)$$

These polynomials can be, of course, obtained very directly by introducing their generating function, but we can avoid doing it by merely noticing that they are simply related, in view of the form of the recursion in Eq.(75), to the so-called golden or Fibonacci polynomials $F_{n+2}(x)$ [39], which are defined by the three-term recursion of the form

$$F_{n+1}(x) = xF_n(x) + F_{n-1}(x), \quad F_1(x) \equiv 1, \quad F_2(x) \equiv x. \quad (76)$$

On comparing the recursions in Eqs.(75) and (76), one infers that

$$K_n(z) = z^{(n+1)/2} F_{n+2}(1/\sqrt{z}). \quad (77)$$

Hence, the approximant \mathcal{F}_n can be expressed as

$$\mathcal{F}_n = \frac{1}{2} \ln(z) + \ln \left(\frac{F_{n+2}(1/\sqrt{z})}{F_{n+1}(1/\sqrt{z})} \right). \quad (78)$$

Note that even at this stage one may understand where from such functions as ϕ_z appear in the expression for the disorder-average pressure in Eq.(53) (first term on the rhs). The point is that, similarly to the Fibonacci numbers $F_n \equiv F_n(1)$, which obey $\lim_{n \rightarrow \infty} F_n/F_{n-1} = \phi_1 = (\sqrt{5} + 1)/2$, the ratio of two consecutive golden polynomials $F_n(1/\sqrt{z})$ and $F_{n-1}(1/\sqrt{z})$ also converges as $n \rightarrow \infty$ to a finite limit given by the function ϕ_z/\sqrt{z} . One expects hence that the rest of terms on the rhs of Eq.(53) stems from the finite- n effects and describes the relaxation of the logarithm of $F_n(1/\sqrt{z})/F_{n-1}(1/\sqrt{z})$ to $\ln(\phi_z)$.

To determine the relaxation terms, one uses the standard definition for the Fibonacci polynomials:

$$F_n(x) = \frac{1}{\sqrt{4+x^2}} \left[\left(\frac{x + \sqrt{4+x^2}}{2} \right)^n - (-1)^n \left(\frac{2}{x + \sqrt{4+x^2}} \right)^n \right] \quad (79)$$

In virtue of this formula, one finds that the ratio of two consecutive golden polynomials obeys

$$\frac{F_{n+2}(1/\sqrt{z})}{F_{n+1}(1/\sqrt{z})} = \frac{\phi_z}{\sqrt{z}} \times \left(\frac{[1 - (-1)^n \omega^{n+2}]}{[1 + (-1)^n \omega^{n+1}]} \right), \quad (80)$$

¹It is straightforward to check that the polynomial $K_n(z)$ is just the partition function in Eq.(1) for a chain of length n in the completely catalytic $p = 1$ system, i.e. $K_n(z) = Z_n(\zeta \equiv 1)$.

where ω has been defined in Eq.(55). Consequently, we find that the n -th approximant \mathcal{F}_n is given by

$$\mathcal{F}_n = \ln(\phi_z) + \ln \left(\frac{[1 - (-1)^n \omega^{n+2}]}{[1 + (-1)^n \omega^{n+1}]} \right), \quad (81)$$

where, as we have already remarked, the first term on the rhs of Eq.(81) corresponds to the limiting form of the approximants, while the second term determines the relaxation to this limiting form; more specifically, to the leading order this relaxation is described by an exponential function $\exp(-n \ln(1/\omega))$. Consequently, one expects a fast convergence in case when z is small (ω is small) and poor convergence when $z \rightarrow \infty$ ($\omega \rightarrow 1$). Substituting Eq.(81) into Eq.(71) we recover, upon some straightforward algebra, the result in Eq.(53).

4.3 Asymptotic behavior of the disorder-average pressure, mean density and the compressibility.

Consider first the small- z behavior of the disorder-average pressure per site, defined by Eq.(53). As we have already remarked, expanding the n -th approximant \mathcal{F}_n into the Taylor series in powers of z , one has that the first n terms of such an expansion coincide with the first n terms of the expansion

$$\ln(\phi_z) = \ln \left(\frac{1 + \sqrt{1 + 4z}}{2} \right) = -\frac{1}{2\sqrt{\pi}} \sum_{n=1}^{\infty} \frac{(-1)^n \Gamma(n + 1/2)}{\Gamma(n + 1)} \frac{(4z)^n}{n}, \quad (82)$$

which implies that \mathcal{F}_n and \mathcal{F}_{n-1} differ only by terms of order z^n and allows to obtain very directly a convergent small- z expansion of the pressure $P_{\infty}^{(quen)}$. We find then

$$\begin{aligned} \beta P_{\infty}^{(quen)} &= z - \left(\frac{1}{2} + p \right) z^2 + \left(\frac{1}{3} + 2p + p^2 \right) z^3 - \\ &- \left(\frac{1}{4} + \frac{7}{2}p + 4p^2 + p^3 \right) z^4 + \mathcal{O}(z^5). \end{aligned} \quad (83)$$

Consequently, in the small- z limit the mean density obeys

$$n_{\infty}^{(quen)} = z - (1 + 2p)z^2 + (1 + 6p + 3p^2)z^3 - (1 + 14p + 16p^2 + 4p^3)z^4 + \mathcal{O}(z^5), \quad (84)$$

while the compressibility $k_T^{(quen)}$ follows

$$\beta^{-1} k_T^{(quen)} = \frac{1}{z} + p(2 - p)z - 4p(2 - p)z^2 + 3p(8 - p - 2p^2)z^3 + \mathcal{O}(z^4). \quad (85)$$

Note now that the expressions in Eqs.(83) to (85) differ from their counterparts obtained in the *annealed* disorder case, Eqs.(21), (24) and (25), only starting from the terms proportional to the fourth power of the activity z . On the other hand, the coefficients in the small- z expansion

nonetheless coincide with the coefficients in the expansions of $P_\infty^{(lan)}$ and $P_\infty^{(reg)}$ when we set in Eq.(83) $p = 0$ or $p = 1$.

Now, we turn to the analysis of the large- z behavior which is a bit more complex than the $z \ll 1$ case and requires understanding of the asymptotic behavior of the sum

$$S = \sum_{N=1}^{\infty} p^N \ln \left(1 - (-1)^N \omega^{N+2} \right) \quad (86)$$

entering Eq.(71). We note first that in this sum the behavior of the terms with odd and even N is quite different and we have to consider it separately.

Let

$$S_{odd} = \frac{1}{p} \sum_{N=1}^{\infty} p^{2N} \ln \left(1 + \omega^{2N+1} \right) \quad (87)$$

denote the contribution of the terms with odd N . Note that when $z \rightarrow \infty$ (i.e. $\omega \rightarrow 1$) the sum S_{odd} tends to $p \ln(2)/(1 - p^2)$. The corrections to this limiting behavior can be defined as follows. Expanding the logarithm $\ln \left(1 + \omega^{2N+1} \right)$ into the Taylor series in powers of ω and then, using the definition $\omega = 1 - 1/\phi_z$ and the binomial expansion, we construct a series in the inverse powers of ϕ_z . This yields

$$\begin{aligned} S_{odd} &= \frac{p}{1 - p^2} \ln(2) - \frac{1}{2} \frac{p(3 - p^2)}{(1 - p^2)^2} \frac{1}{\phi_z} + \\ &+ \frac{1}{8} \frac{p(3 + 6p^2 - p^4)}{(1 - p^2)^3} \frac{1}{\phi_z^2} + \frac{1}{24} \frac{p(15 + 10p^2 - p^4)}{(1 - p^2)^3} \frac{1}{\phi_z^3} + \mathcal{O}\left(\frac{1}{\phi_z^4}\right). \end{aligned} \quad (88)$$

Note that this expansion is only meaningful when $\phi_z \gg (1 - p)^{-1}$, ($z \gg (1 - p)^{-2}$), which signifies that $p = 1$ is also a special point for the quenched disorder case.

Further on, plugging into the latter expansion the definition of ϕ_z , $\phi_z = (1 + \sqrt{1 + 4z})/2$, we obtain the following expansion in the inverse powers of the activity z :

$$\begin{aligned} S_{odd} &= \frac{p}{1 - p^2} \ln(2) - \frac{p}{2} \frac{(3 - p^2)}{(1 - p^2)^2} \frac{1}{z^{1/2}} + \\ &+ \frac{p}{8} \frac{(9 - 2p^2 + p^4)}{(1 - p^2)^3} \frac{1}{z} + \frac{p}{48} \frac{(3 - 4p^2 + p^4)}{(1 - p^2)^3} \frac{1}{z^{3/2}} + \mathcal{O}\left(\frac{1}{z^2}\right). \end{aligned} \quad (89)$$

Consider next the sum

$$S_{even} = \sum_{N=1}^{\infty} p^{2N} \ln \left(1 - \omega^{2N+2} \right), \quad (90)$$

which represents the contribution of terms with even N . Note that in contrast to the behavior of S_{odd} , the sum in Eq.(90) diverges when $z \rightarrow \infty$ ($\omega \rightarrow 1$). Since $1 - \omega^{2N+2} \sim 1 - \omega$ for $\omega \rightarrow 1$, we have that in this limit

$$S_{even} \sim \frac{p^2}{1 - p^2} \ln(1 - \omega) \quad (91)$$

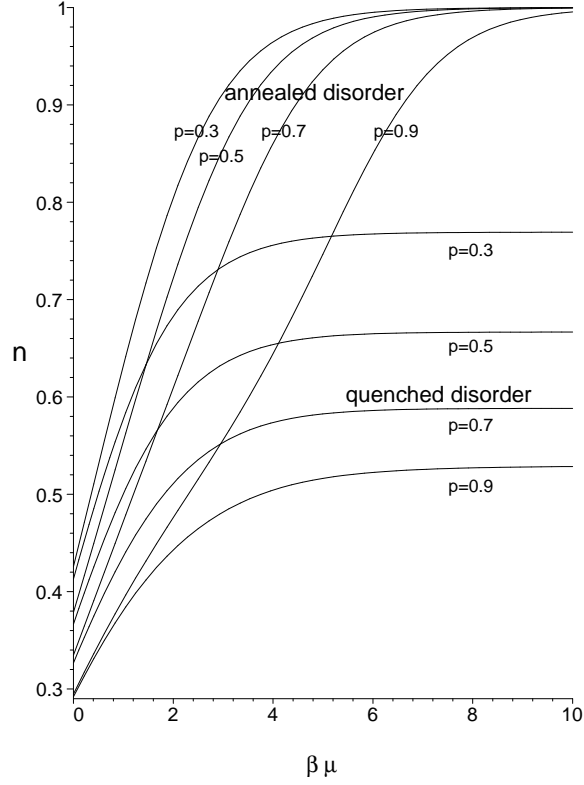


Figure 3: The mean density of adsorbed particles versus the chemical potential $\beta\mu$ for the annealed (curves tending to unity) and quenched disorder case for different values of the mean density p of the catalytic segments.

To obtain several correction terms we make use of one of Gessel's expansions [40]:

$$\ln \left(\frac{2(N+1)x}{1 - (1-x)^{2N+2}} \right) = \sum_{k=1}^{\infty} g_k(2N+2) \frac{(-1)^k x^k}{k}, \quad (92)$$

where $g_k(2N+2)$ are the Dedekind-type sums of the form

$$g_k(2N+2) = \sum_{\zeta^{2N+2}=1, \zeta \neq 1} \frac{1}{(\zeta - 1)^k}, \quad (93)$$

where the summation extends over all ζ being the $(2N+2)$ -th roots of unity (with $\zeta = 1$ excluded). As shown in Ref.[40], the weights $g_k(2N+2)$ are polynomials in N of degree at

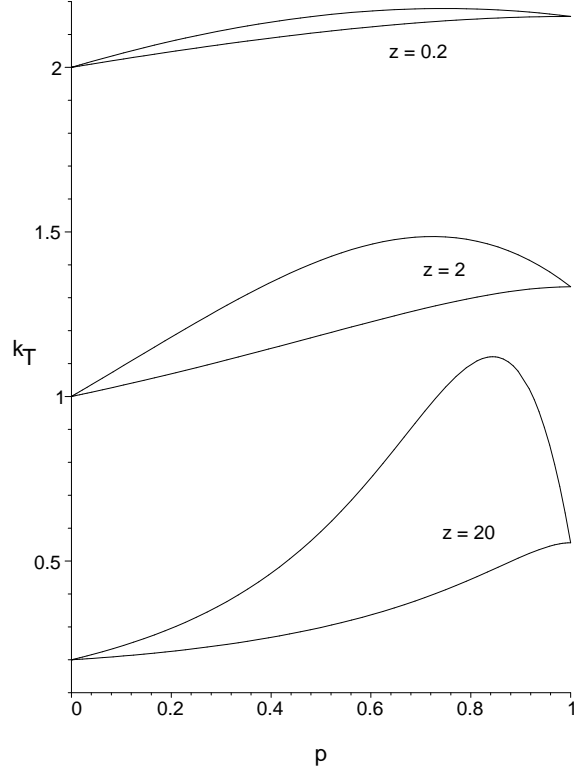


Figure 4: The compressibility $\beta^{-1}k_T$ versus the mean density p of the catalytic segments for several values of the activity z , $z = 0.2, 2$ and $z = 20$. Upper, non-monotoneous curves show the behavior of $\beta^{-1}k_T$ in the *annealed* disorder case, while the lower curves correspond to the solution in the *quenched* disorder case.

most k with rational coefficients; first few values of $g_k(2N + 2)$ are:

$$\begin{aligned}
g_1(2N + 2) &= -(2N + 1)/2, \\
g_2(2N + 2) &= -(2N + 1)(2N - 3)/12, \\
g_3(2N + 2) &= (2N + 1)(2N - 1)/8, \\
g_4(2N + 2) &= (2N + 1)(8N^3 + 28N^2 - 186N + 45)/720.
\end{aligned} \tag{94}$$

Now, setting $x = 1/\phi_z$ in the expansion in Eq.(92), plugging it to Eq.(90) and performing summations over N , we find that S_{even} can be written down as

$$S_{even} = -\frac{p^2}{1-p^2} \ln(\phi_z) + \frac{p^2}{1-p^2} \ln(2) + s_p - \sum_{k=1}^{\infty} G_k(p) \frac{(-1)^k}{k\phi_z^k}, \tag{95}$$

where s_p is an infinite series of the form ²

$$s_p = \sum_{N=1}^{\infty} p^{2N} \ln(N+1), \quad (97)$$

while $G_k(p)$ are the generating functions of the polynomials $g_k(2N+2)$:

$$G_k(p) = \sum_{N=1}^{\infty} g_k(2N+2) p^{2N} \quad (98)$$

Inserting next the definition of ϕ_z , we find the following explicit asymptotic expansion

$$\begin{aligned} S_{even} = & -\frac{1}{2} \frac{p^2}{1-p^2} \ln(z) + \frac{p^2}{1-p^2} \ln(2) + s_p + \\ & - \frac{p^2(2-p^2)}{(1-p^2)^2} \frac{1}{z^{1/2}} + \frac{p^2(21-18p^2+5p^4)}{24(1-p^2)^3} \frac{1}{z} + \frac{p^2(2-p^2)}{24(1-p^2)^2} \frac{1}{z^{3/2}} + \mathcal{O}\left(\frac{1}{z^2}\right). \end{aligned} \quad (99)$$

Finally, combining the expansions in Eqs.(71), (89) and (99), we find the desired large- z expansion for the disorder-averaged pressure $P_{\infty}^{(quen)}$:

$$\begin{aligned} \beta P_{\infty}^{(quen)} = & \frac{1}{1+p} \ln(z) - \frac{(1-p)^2}{(1+p)} \ln(2) + \\ & + \frac{(1-p)^2}{p} s_p + \frac{1}{6} \frac{6+3p-p^3}{(1+p)^2(1-p^2)} \frac{1}{z} + \mathcal{O}\left(\frac{1}{z^2}\right). \end{aligned} \quad (100)$$

Note that $P_{\infty}^{(quen)}$ in Eq.(100) shows a completely different behavior compared to its counterpart in the annealed disorder case already in the leading term in the large- z expansion. Note also that here $p=1$ appears to be a special point and thus the expansion in Eq.(100) becomes meaningless for $p=1$. As a matter of fact, for p arbitrarily close but less than unity one has intervals which are devoid of the catalytic segments. Contribution of such intervals to the overall disorder-average pressure is of a Langmuir-type and vanishes only when p is strictly equal to unity, which implies that also here $p=1$ is a special point.

We find next that for $z \gg (1-p)^{-2}$ the mean particle density obeys

$$n_{\infty}^{(quen)} = \frac{1}{1+p} - \frac{1}{6} \frac{6+3p-p^3}{(1+p)^2(1-p^2)} \frac{1}{z} + \mathcal{O}\left(\frac{1}{z^2}\right), \quad (101)$$

i.e. contrary to the behavior of the mean particle density in the annealed disorder case, Eq.(28), $n_{\infty}^{(quen)}$ tends towards a constant value $1/(1+p)$, which depends on p and coincides

²Note that s_p shows a non-analytic behavior when $p \rightarrow 1$. This function can be represented as

$$s_p = -\frac{1}{1-p^2} \ln(1-p^2) - \frac{p^2}{1-p^2} \sum_{n=2}^{\infty} \frac{(-1)^n}{n} \Phi(p^2, n, 1), \quad (96)$$

where $\Phi(p^2, n, 1)$ are the Lerch transcendent, $\Phi(p^2, n, 1) = \sum_{l=0}^{\infty} (1+l)^{-n} p^{2l}$. It is straightforward to find then that $s_p = -\frac{1}{1-p^2} \ln(1-p^2) - \frac{\gamma}{1-p^2} + \mathcal{O}(\ln(p))$, where γ is the Euler constant.

with the corresponding values $n^{(lan)} = 1$ and $n^{(reg)} = 1/2$ for $p = 0$ and $p = 1$. Behavior of the mean density versus the chemical potential μ for the annealed and quenched disorder cases is presented in Fig.3.

Finally, from Eq.(101) we find that the compressibility $k_T^{(quen)}$ admits the following form:

$$\beta^{-1}k_T^{(quen)} = \frac{1}{6} \frac{6 + 3p - p^3}{(1+p)(1-p^2)} \frac{1}{z} + \frac{1}{36} \frac{p(6 + 3p - p^3)^2}{(1+p)^2(1-p^2)^2} \frac{1}{z^2} + \mathcal{O}\left(\frac{1}{z^3}\right), \quad (102)$$

which expansion also holds in the asymptotic limit $z \gg (1-p)^{-2}$.

5 Conclusions.

To conclude, in this paper we have presented an exact solution of a random reaction/adsorption model, appropriate to the situations with the catalytically-activated reactions on polymer chains containing randomly placed catalyst. More specifically, we have considered here the $A + A \rightarrow 0$ reaction on a one-dimensional regular lattice which is brought in contact with a reservoir of A particles. Some portion of the intersite intervals on the regular lattice was supposed to possess special "catalytic" properties such that they induce an immediate reaction $A + A \rightarrow 0$, as soon as two A particles land onto two vacant sites at the extremities of the catalytic segment, or an A particle lands onto a vacant site while the site at the other extremity of the catalytic segment is already occupied by another A particle. For two different cases; namely, when disorder in placement of the catalytic segments can be viewed as *annealed*, and a more complex situation with a *quenched* random distribution of the catalytic segments, we have determined exactly the disorder-averaged pressure per site. For the annealed disorder case such a pressure has been found in a closed form and explicit asymptotic expansions in powers of the activity for the mean particle density and the compressibility have been obtained. In the case of *quenched* disorder we have shown that the thermodynamic limit result for the disorder-averaged pressure per site can be obtained very directly by noticing a similarity between the expressions defining the pressure in the model under study and the Lyapunov exponent of a product of random two-by-two matrices, obtained by Derrida and Hilhorst [21]. We have also derived an explicit expression obeyed by the averaged logarithm of the partition function, which is valid for any chain's length N . From this expression we have constructed the large- N expansion and have shown, in particular, that the first correction to the thermodynamic limit result for the disorder-averaged pressure per site is proportional to the first negative power of N . The leading term in this expansion coincides with the one found from the analysis by Derrida and Hilhorst. Explicit asymptotic expansions for the mean particle density and the compressibility were also derived. We have demonstrated that for low

activities in the annealed and quenched disorder cases the coefficients in the corresponding expansions of the pertinent parameters in the Taylor series in powers of z coincide up to the order z^3 and slightly deviate from each other starting from the fourth order. On the other hand, expansions in inverse powers of z (large- z behavior) are different already in the leading order. Most spectacular difference between the annealed and quenched disorder case have been observed in the behavior of the compressibility: in the annealed disorder case it appears to be a non-monotoneous function of the mean density p of the catalytic segments, while in the quenched disorder case it is a monotonously increasing function of p .

References

- [1] G.C.Bond, *Heterogeneous Catalysis: Principles and Applications* (Clarendon Press, Oxford, 1987); D.Avnir, R.Gutfraind and D.Farin, in: *Fractals in Science*, eds.: A.Bunde and S.Havlin (Springer, Berlin, 1994)
- [2] A.Clark, *The Theory of Adsorption and Catalysis* (Academic Press, New York, 1970) Part II.
- [3] P.J.Feibelman and J.Harris, *Nature* **372**, 135 (1994)
- [4] R.M.Ziff, E.Gulari and Y.Barshad, *Phys. Rev. Lett.* **50**, 2553 (1986); D.Considine, S.Redner and H.Takayasu, *Phys. Rev. Lett.* **63**, 2857 (1989); E.Clement, P.Leroux-Hugon and L.M.Sander, *Phys. Rev. Lett.* **67**, 1661 (1991); J.W.Evans, *Langmuir* **7**, 2514 (1991); K.Krischer, M.Eiswirth and G.Ertl, *J. Chem. Phys.* **96**, 9161 (1992); P. L. Krapivsky, *Phys. Rev. A* **45**, 1067 (1992); J. W. Evans and T. R. Ray, *Phys. Rev. E* **47**, 1018 (1993); M.Bär, N.Gottschalk, M.Eiswirth and G.Ertl, *J. Chem. Phys.* **100**, 1202 (1994); D. S. Sholl and R. T. Skodje, *Phys. Rev. E* **53**, 335 (1996); Yu. Suchorski, J. Beben, R. Imbihl, E. W. James, D.-J. Liu, and J. W. Evans, *Phys. Rev. B* **63**, 165417 (2001); M. Mabilia and P.-A. Bares, *Phys. Rev. E* **63**, 036121 (2001); P. Argyrakis, S. F. Burlatsky, E. Clément, and G. Oshanin, *Phys. Rev. E* **63**, 021110 (2001)
- [5] J.Marro and R.Dickman, *Nonequilibrium Phase Transitions in Lattice Models*, (Cambridge University Press, Cambridge, 1999)
- [6] A.A.Ovchinnikov and Ya.B.Zeldovich, *Chem. Phys.* **28**, 215 (1978); S.F.Burlatsky, *Theor. Exp. Chem.* **14**, 343 (1978); D.Toussaint and F.Wilczek, *J. Chem. Phys.* **78**, 2642 (1983); K.Kang and S.Redner, *Phys. Rev. Lett.* **52**, 955 (1984); J.Klafter, G.Zumofen and A.Blumen, *J. Phys. Lett. (Paris)* **45**, L49 (1984); K.Lindenberg, B.J.West and R.Kopelman, *Phys. Rev. Lett.* **60**, 1777 (1988); M.Bramson and J.L.Lebowitz, *Phys.*

- Rev. Lett. **61**, 2397 (1988); K.Lindenberg, B.J.West and R.Kopelman, Phys. Rev. A **42**, 890 (1990); W.-S. Sheu, K.Lindenberg and R.Kopelman, Phys. Rev. A **42**, 2279 (1990); M.Bramson and J.L.Lebowitz, J. Stat. Phys. **62**, 297 (1991); S.F.Burlatsky, A.A.Ovchinnikov and G.Oshanin, Sov. Phys. JETP **68**, 1153 (1989); S.F.Burlatsky and G.Oshanin, J. Stat. Phys. **65**, 1095 (1991)
- [7] A.Blumen, J.Klafter and G.Zumofen, in Optical Spectroscopy of Glasses, edited by I.Zschokke (Reidel Publ. Co., Dordrecht, Holland, 1986)
- [8] G.Oshanin, M.Moreau and S.F.Burlatsky, Adv. Colloid and Interface Sci. **49**, 1 (1994)
- [9] G.Oshanin and S.F.Burlatsky, J. Phys. A, to appear; cond-mat/0209656
- [10] S.F.Burlatsky and M.Moreau, Phys. Rev. E **51**, 2363 (1995)
- [11] G.Oshanin and A.Blumen, J. Chem. Phys. **108**, 1140 (1998)
- [12] S.Toxvaerd, J. Chem. Phys. **109**, 8527 (1998)
- [13] G.Oshanin, S.F.Burlatsky, E.Clément, D.Graff and L.M.Sander, J. Phys. Chem. **98**, 7390 (1994)
- [14] J.-M. Park and M. W. Deem, Eur. Phys. J. B **10**, 35 (1999)
- [15] V.A.Benderskii et al, Sov. Phys. JETP **43**, 268 (1976); Phys. Status Solidi B **95**, 47 (1979)
- [16] A.Tretyakov, A.Provata and G.Nicolis, J. Phys. Chem. **99**, 2770 (1995)
- [17] S.Prakash and G.Nicolis, J. Stat. Phys. **82**, 297 (1996); **86**, 1289 (1997)
- [18] F.Vikas, F.Baras and G.Nicolis, Phys. Rev. E **66**, 036133 (2002)
- [19] A.A.Lushnikov, Phys. Lett. A **120**, 135 (1987); C.R.Doering and D.ben-Avraham, Phys. Rev. A **38**, 3035 (1988); M.A.Burschka, C.R.Doering and D.ben-Avraham, Phys. Rev. Lett. **63**, 700 (1989); F.Family and J.Amar, J. Stat. Phys. **65**, 1235 (1991); E.Abad, H.L.Frisch and G.Nicolis, J. Stat. Phys. **99** (2000)
- [20] S.B.Yuste and K.Lindenberg, Phys. Rev. Lett. **87**, 118301 (2001); Chem. Phys. **284**, 169 (2002)
- [21] B.Derrida and H.Hilhorst, J. Phys. A **16**, 2641 (1983)
- [22] C.Domb, Nuovo Cimento **9**, 9 (1958)

- [23] H.N.V.Temperley, Proc. Phys. Soc. (London) **74**, 183, 432 (1959); **77**, 630 (1961); **80**, 813 (1962)
- [24] D.Levesque and L.Verlet, Phys. Lett. **11**, 36 (1964)
- [25] B.Jancovici, Physica **31**, 1017 (1965)
- [26] D.S.Gaunt and M.E.Fisher, J. Chem. Phys. **43**, 2840 (1965)
- [27] L.K.Runnels, L.L.Coombs and J.P.Salvant, J. Chem. Phys. **47**, 4015 (1967)
- [28] R.J.Baxter, J. Phys. A **13** L61, (1980); R.J.Baxter, I.G.Enting and S.K.Tsang, J. Stat. Phys. **22**, 465 (1980); R.J.Baxter, *Exactly Solved Models in Statistical Mechanics*, (Academic Press, New York, 1982); R.J.Baxter, Ann. Combin. **3**, 191 (1999)
- [29] J.W.Evans, Rev. Mod. Phys. **65**, 1281 (1993)
- [30] J.R.Heringa, H.W.J.Blöte and E.Luijten, J. Phys. A **33**, 2929 (2000)
- [31] A.Crisanti, G.Paladin and A.Vulpiani, *Products of Random Matrices in Statistical Physics*, (Springer-Verlag, Berlin, Heidelberg, 1993)
- [32] C.Sire and P.Krapivsky, J. Phys. A **34**, 9065 (2001)
- [33] A.Comtet and S.Nechaev, J. Phys. A **31**, 5609 (1998)
- [34] R.Lima and M.Rahibe, J. Phys. A **27**, 3427 (1994)
- [35] B.McCoy and T.T.Wu, Phys. Rev. **176**, 631 (1968); **188**, 982 (1969)
- [36] H.Furstenberg, Trans. Am. Math. Soc. **108**, 377 (1963)
- [37] H.S.Wilf, Generatingfunctionology, (Academic Press, Inc., 1994)
- [38] B.D.Hughes, *Random Walks and Random Environments*, (Oxford Science Publ., Oxford, 1995)
- [39] R.Honsberger, *A Second Look at the Fibonacci and Lucas Numbers.*, in: Mathematical Gems III. (Washington, DC, Math. Assoc. Amer., 1985); see also: <http://mathworld.wolfram.com/FibonacciPolynomial.html>
- [40] I.M.Gessel, The Electronic Journal of Combinatorics **4**, R11 (1997)